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Surface-induced dechlorination of FeOEP-Cl on Cu(111)

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In the last decades the size of integrated circuit components is shrinking and is on the verge of reaching the scale of single molecules. Therefore, molecular-based devices on the nanoscale have attracted the attention of the scientific community.^[1-4] Metalloporphyrins which form the active centers of many biochemical relevant molecules like chlorophyll, hemoglobin and cytochrome as well as phthalocyanines are two outstanding classes of quasi-planar complexes often used in organic electronic devices.^[5-7] Both macrocyclic pigments exhibit a large variety of electronic and photonic properties and are available in many different forms.^[8-9] Phthalocyanines and porphyrins have in common the four pyrrol rings with one azanitrogen per ring as complex ligand which is able to carry a (transition) metal ion as its molecular core. By the choice of the central metal atom the electronic properties of the molecule can be tuned.

The selfassembly of porphyrins and phthalocyanines was studied on various metallic surfaces.^[10-14] Beside the orientation, i.e. adsorption geometry and the ordering of the molecules, other functional aspects like building a molecular rotor^[12] or switching between different states^[13] were addressed.^[1,15-17]

If iron is the central atom in the porphyrin molecule it can change between the +2 and the +3 oxidation state, e.g. the transport of oxygen in the blood relies on the oxidation of the iron atom and the binding of oxygen molecules in the form of superoxid. The change of the oxidation state is interesting for various reasons. It is accompanied by the modification of the spin state and the magnetic properties of the molecule.^[18-19]

The present study addresses the interaction of Fe-OEP-Cl with a surface, which leads to the partial dechlorination and thereby a change of the oxidation state. It is found, that when FeOEP-Cl molecules are sublimated onto a Cu(111) surface,

two different molecular species are observed by scanning tunneling microscopy even if the sample surface is cooled to 80K during the deposition of the molecules. The central part of the molecule appears in STM images either as a protrusion (type A) or a depression (type B). In combination with van-der Waals corrected DFT-calculations type A is identified as a FeOEP-Cl molecule with the chlorine atom, while type B corresponds to the FeOEP without it. This interpretation is corroborated by a manipulation experiment revealing that it is possible to transform type A into type B by applying a voltage pulse with the STM tip placed over the central part of the molecule.

The chemical structure of the 2,3,7,8,12,13,17,18-octaethylporphyrin Fe(III) chloride formula and the corresponding dechlorinated form are given in Figure 1(a) and (b). FeOEP-Cl (C₃₆H₄₄ClFeN₄) have atomic masses of 624u (50%), 625u (20%), 626u (22%) and 627u (7%). It consists of a porphyrin core with eight ethyl groups attached. In addition, a Cl atom is ligated to the central Fe atom.

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Figure 1. (a) Structural formula of 2,3,7,8,12,13,17,18-octaethylporphyrin Fe(III) chloride (FeOEP-Cl). The chlorine atom points out of the drawing plane. (b) Structural formula of the dechlorinated FeOEP (c) Mass spectra of the source using different electron energies (70, 80 and 90 eV) for electron impact ionization. The spectra reveal that at least 60% or more of the molecules subliming from the source are intact FeOEP-Cl.

Figure 1(c) shows mass spectra obtained when the octaethylporphyrin Fe(III) chloride molecule are thermally evaporated. The temperature of the source is about 500 K and the electron energies for the ionisation are varied between 70, 80 and 90 eV. Since for other porphyrin Fe(III) chlorides the dechlorination by electron impact is very likely^[20], it is expected for the given porphyrin as well. The variation of the fraction of dechlorinated vs. chlorinated molecules as function of the

Figure 2. (a) Topography ($V_{\text{sample}} = -1$ V, $I = 75$ pA, $T = 80$ K) of FeOEP-Cl molecules on the Cu(111) surface deposited at 80 K. Two types of molecules can be distinguished. The A type exhibits a protrusion; the B type a depression at the center as indicated by the arrows for two molecules. Inset: The dotted lines indicate the rows of densely packed copper atoms of the Cu(111) surface. (b) Topography ($V_{\text{sample}} = -1$ V, $I = 75$ pA, $T = 80$ K) of FeOEP molecules in the vicinity of a steps edge on the Cu(111). Again both types of molecules are found. However, in contrast to the free terrace the majority of molecules are of type B at the step edge.

electron energy yields a direct evidence. For the lowest energy the dominant peak is given by the intact molecule at 624 amu. The percentage observed by the mass spectrometer yields an upper limit of 40% for the amount of dechlorinated molecules. Hence, it cannot be excluded that all the molecules leave the source intact.

Figure 2(a) shows the STM image of about 40 molecules adsorbed on the Cu(111) surface. Two different species can be clearly distinguished. One shows a protrusion in the center part (A), the other exhibits a depression (B). On the flat Cu(111)

terrace the ratio of A to B molecules is 85% to 15%. However, images including step edges, e.g. Figure 2(b), reveal that the inverse ratio is approximately found at step edges. In total an average ratio of about 1:1 is found when large areas with about 1500 molecules are analyzed. At higher coverage the step edges are saturated and the ratio approaches 1:1 for the free terrace.

STM data at 80 K show a high tendency of the molecules to move on the surface while imaging. When interacting with the tunneling tip the molecules are very likely to displace or even to be picked up by the tip. Especially, imaging the unoccupied states (positive sample voltage) is almost impossible. The two species of the molecule are found to differ in their likeliness to interact with the tip. The B type tends to be manipulated more easily with the tip than the A type.

Since the A species exhibits a protrusion in the center, we assume that it corresponds to the chlorinated FeOEP-Cl with the chlorine atom pointing upwards. In order to confirm this assignment DFT-simulations of FeOEP-Cl on Cu(111) were performed revealing that the lowest energy is found if the molecule is adsorbed at the bridge-site with the chlorine atom pointing away from the surface. Configurations with the chlorine atom pointing towards the surface are energetically less favorable by at least 1.6 eV, which is very unlikely to be found. The minimal energy is given by two configurations of the ethyl groups, either all of them are pointing up (away from the surface, all-up-state) or half of them are pointing up and the other half down (up-down-state). The all-up-state is the energetically lowest state and is aligned with a molecular symmetry axis to the underlying copper substrate, while the up-down-state is energetically less stable ($\Delta E=0.4\text{eV}$) and is rotated by 15° relative to the substrate.

Accordingly, most of the FeOEP-Cl molecules (~98%) are found in the all-up-state. Figure 3(a-d) displays a comparison between simulated STM images based on the Tersoff-Hamann

approximation and high resolution STM images. The agreement between the measurement and the calculation strongly supports the given assignment. However, there is a minor difference, mainly two opposing pairs of the ethyl groups appear slightly higher (lower) in contrast to the predicted fourfold symmetry. The STM images exhibiting molecular as well as atomic resolution (see Figure 2(a)-inset) confirm the alignment of the molecules to the copper substrate (as indicated by the dotted lines) given by the DFT calculation predicting the absorption at a bridge site.

The B species is identified as the dechlorinated FeOEP. This is strongly supported by the comparison between the DFT-calculation Figure 3(e) for the molecule adsorbed at the bridge site and the STM image Figure 3(f). The up-down-state for the FeOEP has not been observed.

The comparison of subsequent images shows that the dechlorinated FeOEP molecules diffuse more easily on the surface. At 80 K this may be partially induced by the interaction with the tunneling tip. The thermal diffusion can be verified by heating the sample for a short time. The STM images after this procedure show that only chlorinated molecules are found on the free terrace, while the dechlorinated diffused to the step edges.

To further corroborate the identification of the two molecular species, we performed an STM manipulation experiment detaching the Cl-ligand of the molecule displayed in Fig. 3d.^[21] With a probability in the order of 30 % this can be achieved by raising the voltage from -1 V to -2.5 V at constant distance for a duration of 100 ms at the center of a type A molecule. By this procedure the central protrusion is removed and the type A molecule is modified to type B, as can be seen in Figure 4. Since it is expected that the voltage pulse detaches the chlorine atom^[22] of the molecule and the resulting species appears identical to

Figure 3 (two column). For all images the underlying Cu(111) substrate is oriented with one of the lattice vectors (row of copper atoms) in the vertical direction. (a-b) Simulated STM image based on DFT calculations for FeOEP-Cl ($eV_{\text{sample}}=-1\text{ eV}$) at the energetically lowest state and experimental obtained data ($V_{\text{sample}}=-1\text{ V}$, $I=60\text{ pA}$, $T=80\text{ K}$) for the all-up configuration (c-d) Simulated and experimental data ($V_{\text{sample}}=-1\text{ V}$, $I=60\text{ pA}$, $T=80\text{ K}$) for the energetically less stable up-down state ($\Delta E=0.4\text{eV}$). (e-f) Simulated STM images and experimental data for FeOEP ($eV_{\text{sample}}=-1\text{ eV}$) for the energetically lowest all-up state. (g) Simulated data for

FeOEP for the energetically less stable up-down state ($\Delta E=0.6\text{eV}$). (h) Scheme of both different states: The all-up state with 8 ethyl groups pointing upwards and the up-down configuration in which neighboring ethyl groups are pairwise pointing up or downwards.

type B, the latter is identified as the dechlorinated FeOEP molecule. For the given example the dechlorination goes along with the change from the “up-down” to the “all-up” configuration. Hence a rotation of about 15° is observed.

Since FeOEP-Cl molecules leave the molecular source intact or at maximum 40% are dechlorinated, but more dechlorinated molecules are found on the Cu(111) surface, the dechlorination happens at least partially at the surface. Two plausible mechanisms are proposed:

- I. The dechlorination is induced by the step edges. Thus, the dechlorination happens after the adsorption of the molecules on the surface. That may explain why most of the dechlorinated FeOEP molecules are found at the step edges.
- II. Those molecules which arrive at the surface with the chlorine atom facing the surface react by breaking the bond between the Cl atom and the FeOEP molecule. This seems likely since the DFT calculation reveals that the adsorption with the Cl-atom pointing down is energetically very unfavorable. In contrast to mechanism I the dechlorination process would happen during the adsorption of the molecules on the surface. If one assumes that the molecules are not dechlorinated in the source this could well explain why in average over the whole surface about an equal number of both species is found.

Figure 4. (a-b) STM images before and after the dechlorination process ($V_{\text{sample}}=-1\text{ V}$, $I=100\text{ pA}$, $T=80\text{ K}$). Applying a voltage pulse of $V=-2.5\text{ V}$ for $t=100\text{ ms}$ at the core of the A type molecule removes the Cl-ion. (c) shows linescans across the center of the molecule.

The ratio between chlorinated and dechlorinated molecules is 1:1 for adsorption at sample temperatures of 80 K as well as 300 K. Since this seems to be a rather robust number, we propose mechanism II; i.e. the dechlorination happens during the adsorption process. There are some indications, e.g. by fuzzy STM images, that the desorbed chlorine atoms remain on the copper surface, as reported in previous publications.^[23-24]

In summary, after the adsorption approximately 0.1 of a monolayer of FeOEP-Cl onto the cooled Cu(111) surface (80 K), two species of FeOEP molecules are observed by our LT-STM study. By comparison to DFT calculation we identify the species with a central protrusion as the intact FeOEP-Cl molecule with the Cl atom oriented away from the surface. The other species with a central depression is the dechlorinated FeOEP. The majority of the individual molecules adsorbed on the terraces

are FeOEP-Cl molecules, while the molecules bound to atomic steps are mainly dechlorinated FeOEP molecules.

Experimental Section

Experimental

The experiments were performed using a self-built combined low temperature scanning tunneling microscope/atomic force microscope (LT-STM/AFM)^[25] operated in ultra-high vacuum at $T=80\text{ K}$. The Cu(111) substrate was prepared by several cycles of Ar^+ -sputtering and annealing at about 900 K. The molecules are sublimated from a self-built transferable furnace.^[26] Prior to the deposition of the molecules onto the surface, the flux of molecules from the source was studied by means of a quadrupole mass spectrometer (Pfeiffer QMS 422) with a mass range of up to 1024 amu. To prepare the sample surface the source was placed close to the STM. Approximately 0.1 of a monolayer of FeOEP-Cl was deposited onto the sample directly into the cooled microscope at $T=80\text{ K}$.

The tunneling tips were prepared by electrochemical etching of a tungsten wire with a diameter of 0.1 mm. The apex of the tip is prepared *in situ* by field emission of electrons at about 200 V and further voltage pulses. The tunneling current is measured at the tip, the tunneling voltages is applied to the sample. STM data were acquired using the open source software GxSM^[27] and furthermore processed using WSxM.^[28]

Theoretical

Ab initio electronic structure calculations were performed within the density functional theory (DFT) framework as implemented in the VASP code.^[29] Core electrons were treated in the projector augmented wave method (PAW)^[30], and wavefunctions were expanded using plane-waves with a cutoff energy of 350 eV. The generalized gradient approximation in the PBE^[31] form was used for the exchange and correlation functional. To account for correlation effects missed in conventional DFT, we have applied a GGA+U^[32] correction to the Fe d electrons, with $U_{\text{eff}}=U-J=3\text{ eV}$.

This value has been previously shown to be adequate for these molecules.^[14] The missed long range van der Waals interactions between molecules and the Cu surface have been included using the DFT+D2 scheme of Grimme,^[33] which has been shown to give good results for similar supported molecules.^[34] The Cu(111) surface have been simulated using a four layer slab. The first Cu layer and the molecules were relaxed until the forces were below $0.05\text{ eV}\text{\AA}^{-1}$.

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